

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
25 November 2004 (25.11.2004)

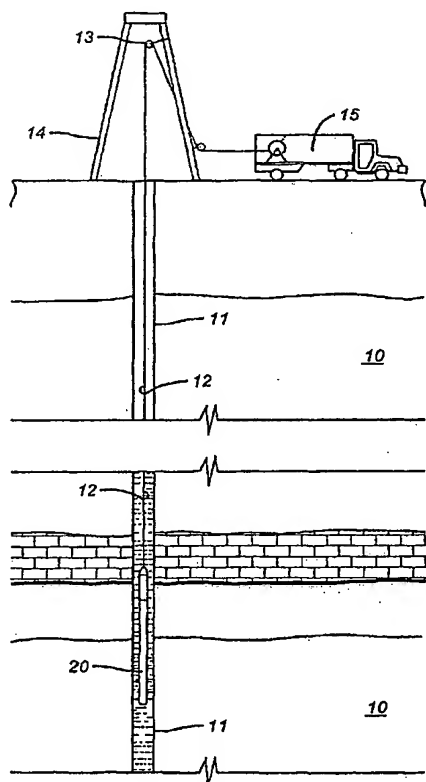
PCT

(10) International Publication Number  
**WO 2004/102169 A1**

- (51) International Patent Classification<sup>7</sup>: G01N 21/39, G01V 8/00, G02B 26/10
- (21) International Application Number: PCT/US2004/013887
- (22) International Filing Date: 5 May 2004 (05.05.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/468,372 6 May 2003 (06.05.2003) US
- (71) Applicant (for all designated States except US): **BAKER HUGHES INCORPORATED** [US/US]; 3900 Essex Lane, Suite 1200, Houston, TX 77027 (US).
- (72) Inventor: **DIFOGGIO, Rocco**; 12006 Plumpoint Dr., Houston, TX 77099 (US).
- (74) Agents: **RIDDLE, Albert, J. et al.**; Baker Hughes Incorporated, Suite 1200, 3900 Essex Lane, Houston, TX 77027 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,

[Continued on next page]

(54) Title: METHOD AND APPARATUS USING A TUNABLE DIODE LASER SPECTROMETER FOR ANALYSIS OF HYDROCARBON SAMPLES



(57) Abstract: The present invention provides an down hole apparatus and method for ultrahigh resolution spectroscopy using a tunable diode laser (TDL) for analyzing a formation fluid sample downhole or at the surface to determine formation fluid parameters. In addition to absorption spectroscopy, the present invention can perform Raman spectroscopy on the fluid, by sweeping the wavelength of the TDL and detecting the Raman-scattered light using a narrow-band detector at a fixed wavelength. The spectrometer analyzes a pressurized well bore fluid sample that is collected downhole. The analysis is performed either downhole or at the surface onsite. Near infrared, mid-infrared and visible light analysis is also performed on the sample to provide an onsite surface or downhole analysis of sample properties and contamination level. The onsite and downhole analysis comprises determination of aromatics, olefins, saturates, gas oil ratio, API gravity and various other parameters which can be estimated by correlation, a trained neural network or a chemometric equation.

WO 2004/102169 A1

BEST AVAILABLE COPY



SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**Published:**

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

**A METHOD AND APPRATUS<sup>1</sup> FOR A TUNABLE DIODE LASER  
SPECTROMETER FOR ANALYSIS OF HYDROCARBON SAMPLES**

**Cross Reference to Related Applications**

This patent application is a continuation in part and claims priority from U.S. Provisional Patent Application serial number 60/468,372 filed on May 6, 2003 entitled "A Method and Apparatus for a Tunable Diode Laser Spectrometer for Analysis of Hydrocarbon Samples," by Rocco DiFoggio.

**Background of the Invention**

**Field of the Invention**

The present invention relates generally to the field of downhole sampling and in particular to the downhole and onsite surface ultrahigh resolution spectroscopy using a tunable diode laser for measurement and estimation of parameters of interest of hydrocarbon samples prior to, during, or after capture in a sample chamber.

**Summary of the Related Art**

Typically, sample tanks are transported to laboratories for analysis to determination formation fluid properties based on the sample. The samples have to be transferred to a transportation tank and, in so doing, risk sample damage and spoilage due to pressure loss and formation of bubbles or asphaltene precipitation in the sample. Moreover, even if the sample is transferred successfully, it typically takes weeks or months to receive the laboratory analysis. Thus, there is a need for a quicker sample analysis for downhole in situ analysis and for onsite surface analysis.

Currently spectral analysis downhole or onsite using optical filters is limited to around 11 nm full width half maximum wavelength resolution. These filters are not suitable to distinguish between close peaks, resolve small peaks superimposed on large peaks, or to identity differences in isotopes whose features are much smaller than 11 nm. Thus, there is a need for an analysis technique suitable for downhole and onsite surface spectrographic analysis of hydrocarbon samples with high resolution on the order of 1-4 nm or much better. Manufacturers of tunable diode lasers often claim 0.01 nm or better resolution.

**Summary of the Invention**

The present invention addresses the shortcomings of the related art described above. The present invention provides an apparatus and method for onsite surface and downhole

spectral analysis of formation fluid samples, whether filtrate, hydrocarbon or brine collected downhole in an earth boring or well bore. The present invention provides a tunable diode laser (TDL) for ultrahigh resolution spectroscopy (UHRS) and corresponding estimation of parameters of interest of such samples based on correlation to these UHRS measurements. A sorption cooling apparatus is also provided to cool the TDL and UHRS downhole if necessary. A plurality of TDLs are ganged together in one embodiment to span a hydrocarbon band of frequencies from approximately 1650 nm to 1850 nm or to provide a tunable spectral range over selected areas of interest in selected frequency bands. In a preferred embodiment a TDL for UHRS is provided downhole for real time UHRS measurements and estimation of parameters of interest from the UHRS measurements. In another embodiment the TDL UHRS is performed at the surface onsite or by the UHRS in the tool or via a separate UHRS system attached at the surface. The TDL UHRS of the present invention is also useful for analysis of gases and fluids and isotopes thereof while flowing in distribution pipelines to determine the purity, grade and identity of hydrocarbon bearing fluids and gases.

#### Brief Description of the Figures

For detailed understanding of the present invention, references should be made to the following detailed description of the preferred embodiment, taken in conjunction with the accompanying drawings, in which like elements have been given like numerals, wherein:

**FIG. 1** is a schematic earth section illustrating the invention operating environment;

**FIG. 2** is a schematic of the invention in operative assembly with cooperatively supporting tools;

**FIG. 3** is a schematic of a representative formation fluid extraction and delivery system;

**FIG. 4** is an illustration of a preferred sample chamber and analysis top sub;

**FIG. 5** is an illustration of an alternative embodiment having a water pump to pressurize a sample for analysis by an external unit;

**FIG. 6** is an illustration of a common current analysis procedure;

**FIG. 7** is an illustration of the new improved procedure provided by the present invention;

**FIG. 8** is an illustration of an alternative embodiment;

**FIG. 9** is an illustration of another alternative embodiment;

**FIG. 10** is a schematic illustration of a preferred embodiment of a tunable diode laser spectrometer; and

**Fig. 11** is an example of an alternative embodiment for determining reflectance spectra using a tunable diode laser attached to an optical probe.

#### Detailed Description of an Exemplary Embodiment

The present invention provides an ultrahigh resolution spectrometer using a tunable diode laser to enable high-resolution spectral measurements from which we can estimate the percent of oil-based mud filtrate contamination in crude oil samples. The present invention also enables high-resolution spectral measurements to estimate the mole fraction or percent of chemical groups (aromatics, olefins, saturates) in a crude oil or gas sample or to measure gas oil ratio (GOR).

The present invention provides an ultrahigh resolution spectrometer using a tunable diode laser to enable high-resolution spectral measurements to estimate if a crude oil sample contains dry gas or wet gas (amounts of  $C_1$  relative to amounts of  $C_2$ ,  $C_3$ , and  $C_4$ ). The present invention is also suitable for use in a pipeline, refinery or laboratories. The present invention provides an ultrahigh resolution spectrometer based on a tunable diode laser to enable spectral high-resolution measurements to estimate  $CO_2$  in methane gas or  $CO_2$  dissolved in crude oil.

The present invention provides an ultrahigh resolution spectrometer using a tunable diode laser to enable high-resolution spectral measurements to provide improved correlations to physical properties (API Gravity, cloud point, bubble point, asphaltene precipitation pressure, etc.) or chemical properties (acid number, nickel, vanadium, sulfur, mercury, etc.) of crude oil or  $^{13}C / ^{12}C$  isotope ratios of methane gas.

The present invention provides an ultrahigh resolution spectrometer using a tunable diode laser to enable high-resolution spectral measurements to estimate the phytane / pristane ratios of crude oil.

The present invention provides a membrane to separate water vapor from liquid water for isotope analysis of the vapor. Examples of such membranes include Diaplex polyurethane membranes (Mitsubishi Heavy Industries) and Dermizax polyurethanes from Toray Industries both of which are waterproof yet breathable for permeation by water vapor.

The present invention also provides a membrane (such as a silicone rubber) to separate methane gas from liquid crude oil for gas isotope analysis of the gas. The present invention applies TDL spectroscopy to liquids and to gases dissolved in liquids.

The present invention provides an ultrahigh resolution spectrometer based on a tunable diode laser to enable high-resolution spectral measurement to estimate the  $\text{H}_2\text{S}$  that is dissolved in crude oil. The present invention provides an ultrahigh resolution spectrometer using a tunable diode laser to enable ultrahigh resolution spectral measurements to estimate the  $^{17}\text{O} / ^{18}\text{O}$  isotopes of water. The present invention provides an ultrahigh resolution spectrometer using a tunable diode laser to enable high-resolution spectral measurements to obtain approximate "synthetic" coarse-scale gas chromatograms (envelope of  $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{C}_3$ , etc.). The present invention provides an ultrahigh resolution spectrometer using a tunable diode laser to enable high-resolution spectral measurements to estimate the  $^{13}\text{C} / ^{12}\text{C}$  isotopes of methane gas.

The present invention compensates for small wavelength range of TDLs by using several of these small lightweight sensors (TDLs) in selected wavelength regions. The present invention provides a high-temperature TDL spectrometer or cools an ordinary temperature ( $80^\circ\text{C}$ ) TDL spectrometer with sorption cooling. The present invention provides a TDL to analyze the properties of a formation fluid sample in an optically transparent windowed sample tank. In one embodiment the present invention provides a set of wide-range (100-200 nm) room-temperature or high temperature TDLs centered around the hydrocarbon band (1740 nm).

The present invention provides a high resolution TDL for spectral measurements from which to infer physical and chemical properties of sample formation fluids or other fluids not previously thought possible by spectroscopic means downhole or at the surface. The present invention takes advantage of the TDL's rapid wavelength switching capability to perform high resolution derivative spectroscopy, to for example, find peaks on a shoulder of another peak or to greatly improve signal to noise and makes it possible to observe subtle changes (e.g., 10-20 ppm  $\text{H}_2\text{S}$ ), not possible with lower resolution conventional mid infrared (MIR) & near infrared (NIR) spectroscopy.

The present invention provides a two-pathlength (long and short path lengths) sample cell and a single photodetector so that the cell is self-referenced for absorbance or transmittance readings. The present invention provides a fast beam steering method (e.g., an acousto-optic device or rotating prism, etc.) to shift the TDL beam between the thin (short path length) and thick (long path length) sections of the sample cell. Then, the optical

absorbance for a pathlength that is equal to the difference between the long and short pathlengths is the base ten logarithm of the ratio of the short-path transmitted light intensity to the long-path transmitted light intensity.

The present invention provides a decompressible or evacuable chamber covered by a membrane, which membrane is in contact with the liquid to extract vapor or gas to enable isotope analysis by the TDL spectrometer. The sample chamber flow path can be evacuated by withdrawing a piston to enlarge the chamber volume and lower the pressure within the chamber flow path drawing vapor through the membrane out of the liquid on the opposite side of the membrane.

Tunable diode lasers (TDLs) are provided for ultrahigh resolution spectroscopy (e.g., resolving  $^{13}\text{C}$  methane gas from  $^{12}\text{C}$  methane gas). US Patent no. 5,781,284, "System for detecting impurities contained in a fluid medium," describes using a tunable diode laser, but not for performing a spectral scan. The '284 patent teaches using a TDL to simply modulate a light at 400 Hz so as to distinguish the modulated signal from background. Intensity modulation of a light emitting diode could have served this purpose in US 5,781,284 just as well instead of using a wavelength-modulated TDL.

The advantages of TDLs are their high intensity, extremely fine wavelength tunability, and comparatively small size and weight. Their disadvantages are the small tunable wavelength range over which they operate (4 to 10 nm is common, but increasingly TDLs are available with a tunable operating range of 100 nm or more) and their limited temperature range of operability (usually no more than 80° or 90°C). Thus, the present invention provides a wide operating range TDL or an array of TDLs ganged together to cover a wide wavelength range of coverage and tuning within the range. Preferably, selected wavelength regions such as the hydrocarbon band,  $\text{CO}_2$  band,  $\text{H}_2\text{S}$  band, and the  $\text{H}_2\text{O}$  band are selected for TDL spectral coverage and tuning within these bands. In a preferred embodiment, the present invention spectrally separates isotopes of liquid water or isotopes of methane in a mixture of gases or when either is dissolved in liquid water or crude oil. A laboratory Fourier transform infrared (FTIR) spectrometer typically provides a 100 to 1000 times wider spectral range although an FTIR provides much lower light intensity at each wavelength and much less wavelength resolution. An FTIR laboratory spectrometer typically provides a wavelength resolution of  $1\text{ cm}^{-1}$  ("wave numbers") but TDLs can provide resolution as high as  $10^{-4}\text{ cm}^{-1}$  or  $10^{-5}\text{ cm}^{-1}$ .

TDL spectroscopy is ideal for gas analysis because of its high resolution and ability to resolve the rotational splitting of the vibrational bands. The TDL is rapidly tuned when used for derivative spectroscopy. Thus, the TDL is useful to analyze for highly reactive systems such as free radicals, carbon clusters, ions, various reactive metal compounds, and weakly bound complexes.

Having a higher temperature (perhaps a quantum dot) TDL spectrometer fabricated or combining a tunable diode laser with downhole sorption cooling or other cooling mechanism overcomes temperature issues. For sorption cooling, the tunable diode laser is placed in thermal contact with a source of water (either liquid or as hydrate). The TDL is cooled as the water is evaporated from liquid or released by hydrate. The resulting water vapor is sorbed by a sorbent, which becomes hotter in the process. The sorbent transfers its excess heat to the well bore fluid with which it is in thermal contact through the tool housing.

The present invention quantifies aromatics, olefins (unlikely in crude oil but common in oil-based mud, OBM, filtrate), saturates, methane and quite possibly ethane, propane, and butane. With this high resolution spectroscopy, the present invention determines the percentage of oil based mud filtrate contamination downhole, particularly if the base oil is aromatic-free (unlike crude oil) but olefin-rich (also unlike crude oil).

Furthermore, with very high resolution, the present invention determines the isotopic ratios of methane ( $^{13}\text{C}/^{12}\text{C}$ ) or isotopic ratios of water (for different oxygen isotopes) and quantifies gases such  $\text{CO}_2$  (e.g.,  $1430\text{ nm}=6993\text{ cm}^{-1}$ ,  $1572\text{ nm}=6361\text{ cm}^{-1}$ ,  $1996\text{ nm}=5010\text{ cm}^{-1}$ ,  $2019\text{ nm}=4953\text{ cm}^{-1}$ ) or  $\text{H}_2\text{S}$  (e.g.  $1578\text{ nm} = 6337\text{ cm}^{-1}$ ).

Alternatively, the present invention provides a set of sorption-cooled single-wavelength (not tunable) diode lasers, each at a carefully selected wavelength, to perform spectroscopy at a set of predetermined fixed wavelengths.

Tunable diode lasers (TDLs) are provided for very high resolution spectroscopy for gas and fluids at the surface and downhole. For example, TDLs are provided to quantify one gas in the presence of many others or to quantify different isotopes of the same gas. In one embodiment, by tuning the wavelength of the TDL light source and using a single-



Alternatively, the present invention provides a set of single-wavelength (not tunable) diode lasers, each set at a carefully selected wavelength of interest, to perform spectroscopy at a set of predetermined fixed wavelengths. In another embodiment, a set of tunable TDLs are provided to measure over a set of wavelengths of interest corresponding to wavelengths associated with parameters of interest each TDL being tunable with a selected frequency band.

Turning now to **FIG. 1**, **FIG. 1** schematically represents a cross-section of earth **10** along the length of a wellbore penetration **11**. Usually, the wellbore will be at least partially filled with a mixture of liquids including water, drilling fluid, and formation fluids that are indigenous to the earth formations penetrated by the wellbore. Hereinafter, such fluid mixtures are referred to as "wellbore fluids". The term "formation fluid" hereinafter refers to a specific formation fluid exclusive of any substantial mixture or contamination by fluids not naturally present in the specific formation. Suspended within the wellbore **11** at the bottom end of a wireline **12** is a formation fluid sampling tool **20**. The wireline **12** is often carried over a pulley **13** supported by a derrick **14**. Wireline deployment and retrieval is performed by a powered winch carried by a service truck **15**, for example.

Pursuant to the present invention, an exemplary embodiment of a sampling tool **20** is schematically illustrated by **FIG. 2**. Preferably, such sampling tools comprise an assembly of several tool segments that are joined end-to-end by the threaded sleeves or mutual compression unions **23**. An assembly of tool segments appropriate for the present invention may include a hydraulic power unit **21** and a formation fluid extractor **22**. Below the extractor **22**, a large displacement volume motor/pump unit **24** is provided for line purging. Below the large volume pump is a similar motor/pump unit **25** having a smaller displacement volume that is quantitatively monitored as described more expansively with respect to **FIG. 3**. Ordinarily, one or more sample tank magazine sections **26** are assembled below the small volume pump. Each magazine section **26** may have three or more fluid sample tanks **30**.

The formation fluid extractor **22** comprises an extensible suction probe **27** that is opposed by bore wall feet **28**. Both, the suction probe **27** and the opposing feet **28** are hydraulically extensible to firmly engage the wellbore walls. Construction and operational details of the fluid extraction tool **22** are more expansively described by U.S. Patent No. 5,303,775, the specification of which is incorporated herewith.

Turning now to FIG. 4, in a preferred embodiment of the present invention comprises an optically transparent windowed sample tank referred to herein as an advanced optical cylinder (AOC) 800 which further comprises a pressurized sample tank and analytical top sub 818. The pressurized sample tank comprises a pressure compensation system 810, having a nitrogen pressure chamber 812 provided to apply high pressure on the fluid sample which is sufficient to keep a downhole captured fluid sample 821 in chamber 816 above the bubble point pressure and above the pressure at which asphaltenes precipitate out of the sample. The AOC is also suitable for downhole capture, pressurization and analysis of gas or fluid captured in chamber 816.

The AOC top sub 818 provides one or a pair of high pressure sapphire windows 814 TDL UHRS for optical analysis of parameters of interest for formation fluid sample 821. An analysis module 738 which embodies the preferred TDL UHRS is provided for analysis of the sample downhole or at the surface.

In operation, as show in FIG. 5, the AOC is removed from a sample tank carrier and the sample 821 pressure is stabilized by pumping pressurized water 920 behind the piston 921 using pump 910. At this time nitrogen is released and the nitrogen chamber can be detected from the sample chamber. An external optical analyzer 830 or analysis module 738 comprising the TDL UHRS and preferably an NIR/MIR ultraviolet or visible light source and TDL spectrometers are provided for onsite analysis or downhole analysis. Such analysis performed without disturbing the fluid sample or requiring transferring the sample to another Department of Transportation (DOT) approved chamber for transport to an off-site laboratory for analysis.

The optical analyzer of the present invention preferably uses wavelength ranges from approximately 1500 nm to 2000 nm to scan the fluid sample to determine sample contamination percentage, gas oil ratio (GOR), density and asphaltene deposition pressure. Low resolution conventional spectrometers, a tunable diode laser UHRS and TDL operated in conjunction with a single-wavelength detector for Raman scattered light to perform Raman spectroscopy are also provided for spectral analysis of the fluid sample.

The analysis module 738 embodying the preferred TDL UHRS and associated optical analysis equipment is attached or associated with in the AOC prior to going downhole. While downhole the TDL UHRS is used to perform analysis described herein during a

downhole run or at the surface upon completion of a sampling run downhole. Some of the numerous advantages of the TDL UHRS of the present invention are shown by comparison of FIG. 6, a commonly known system to which FIG. 7 illustrates the new design provided by the TDL UHRS of the present invention. Note that in FIG. 7 that a Primary Parameter Calculation by an optical analysis system is available almost immediately in a relative sense or in less than six hours. A final PVT report is provided by the present invention in less than a week or less rather than six to eight weeks as shown in FIG. 6 for the common system. Moreover, there is no sample transfer required as onsite equipment in both the analysis module 738 and external equipment 830 perform PVT and spectral analysis to determine asphaltene deposition, bubble point, formation volume factor, compositional analysis and additional analysis described herein.

Turning now to FIG. 8 an alternative embodiment of the present invention is presented showing top sub 818 containing analysis module 738 attached to sample chamber 1210 pressurized by nitrogen (N<sub>2</sub>) 1212 and hydrostatic pressure 1214 while downhole. Thus, the present invention performs sampling and TDL UHRS sample analysis while downhole or at the surface.

As shown in FIG. 8, the analysis window unit comprises an analysis module 738, a tunable diode laser spectrometer 1415 and a sorption cooling unit 1416. Sorption cooling unit 1416 is described in co-owned patent application serial number 09/756,764 filed on January 8, 2001 entitled "Downhole Sorption Cooling in Wireline Logging and Monitoring While Drilling" by Rocco DiFoggio, incorporated herein by reference in its entirety. As shown in FIG. 9, an external TDL UHRS 1515 is attached to the AOC to analyze the sample at the surface via external window unit 1510.

The preferred tunable diode laser 1415 spectrometer enables the present invention to perform ultrahigh resolution spectroscopy downhole during or prior to sampling, after sampling or at the surface. Sorption cooling unit 1416 cools is provided if needed adjacent the tunable diode laser and other electronics downhole as necessary to obviate the adverse affects of downhole temperatures.

Turning now to Fig. 10 a preferred embodiment of the present invention is shown. In a preferred embodiment, a TDL 1608 or multiple TDLs 1609 are provided along with a spectral detector 1606 or multiple spectral detectors 1606a. A processor is provided for

controlling the TDL, controlling all electronics such as the color shifter 1603, and for reading sampling or measuring detector 1606. The processor also controls beam deflector 1610 to deflect a beam from TDL between the short sample flow path 1604 and the long sample flow path 1602 to determine the ratio between the two paths. A single-wavelength detector 1603 is provided to perform Raman spectroscopy of the fluid and to enable detection of nitrogen and other infrared inactive components in a gas or liquid sample.

The additional TDLs 1609 are selected at wavelengths of interest to analyze the sample for peaks relating to a measureable spectral component or to estimate a parameter of interest from the selected measured components. A trained neural network or chemometric equation resident in the processor 1611 and developed based on a correlation between parameters of interest and measured spectral content is used to estimate parameters of interest (GOR, API gravity, etc.) for the fluid or gas sample for which the TDL is used to measure spectral content.

Membrane 1616 is optionally provided to separate liquid from vapor in the sample flow path when desired. Piston 1617 is provided to evacuate the sample flow path 1600 to pull vapor into the sample flow path past the membrane 1616 for analysis of gas only in the flow path.

Turning now to Fig. 11, in an alternative example of the invention, tunable diode laser spectrometer probe 1110 is inserted into the sample 821 to transmit from TDL source 1611 and to receive returned light using receiver 1612 to determine optical characteristics for the sample 821. TDL source and receiver 1646 transmits light through optical window 814 to the interface 1111 between the sample 821 and the window 814 to measure light reflected off of the liquid window interface 1111 to determine reflectance spectra of the sample..

In another embodiment, the method of the present invention is implemented as a set computer executable of instructions on a computer readable medium, comprising ROM, RAM, CD ROM, Flash or any other computer readable medium, now known or unknown that when executed cause a computer to implement the method of the present invention.

While the foregoing disclosure is directed to the preferred embodiments of the invention various modifications will be apparent to those skilled in the art. It is intended that all variations within the scope of the appended claims be embraced by the foregoing.

disclosure. Examples of the more important features of the invention have been summarized rather broadly in order that the detailed description thereof that follows may be better understood, and in order that the contributions to the art may be appreciated. There are, of course, additional features of the invention that will be described hereinafter and which will form the subject of the claims appended hereto.

## Claims

1. An down hole apparatus for monitoring a parameter of interest for a fluid sample comprising:  
a down hole tool containing a chamber for containing a fluid sample; and  
a tunable diode laser spectrometer for analyzing the fluid sample to determine a first parameter of interest for the fluid sample.
2. The apparatus of claim 1, further comprising :  
a membrane for separating vapor from liquid for isotope analysis of vapor.
3. The apparatus of claim 1, further comprising:  
a plurality of tunable diode lasers for analyzing a band of frequencies associated with the fluid sample.
4. The apparatus of claim 1, further comprising:  
wherein the tunable diode laser combined with a single-wavelength detector serves as a Raman spectrometer for analyzing the fluid sample.
5. The apparatus of claim 1, further comprising:  
a neural network, chemometric equation or least mean squares fit for estimating a parameter of interest from the tunable diode laser spectrometer measurements.
6. The apparatus of claim 4, wherein Raman spectroscopy is performed by tuning the wavelength of light that enters the sample and measuring the Raman-shifted light using a single-wavelength detector.
7. The apparatus of claim 1, wherein the tunable diode laser wavelength is modulated at high frequency to create a derivative spectrometer.
8. The apparatus of claim 1, further comprising:  
a neural network for estimating a second parameter of interest for the fluid sample from a first parameter of interest of the fluid sample.

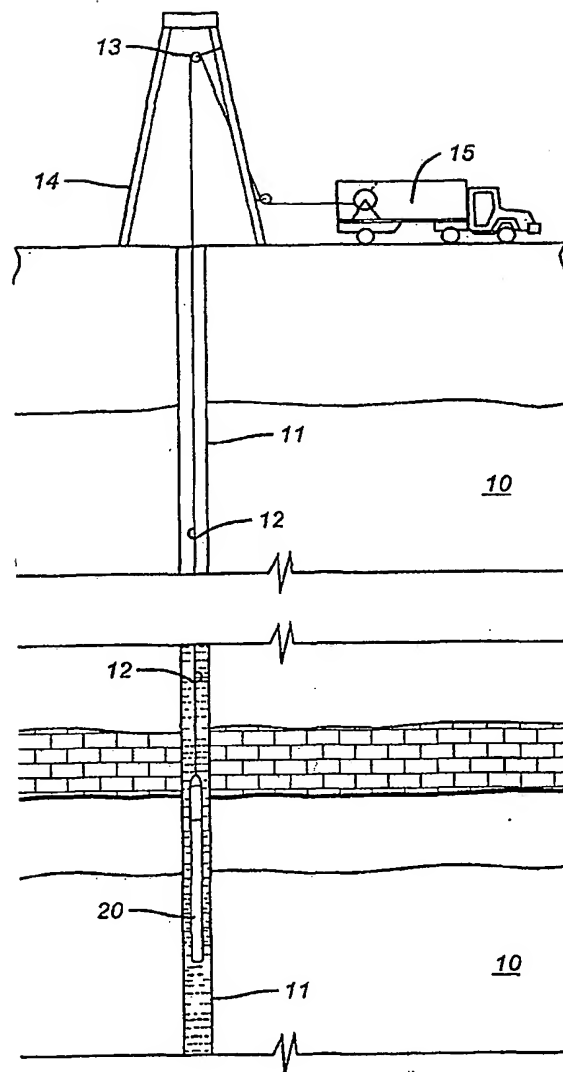
9. The apparatus of claim 1, further comprising:  
a chemometric equation for estimating a second parameter of interest for the fluid sample from the first parameter of interest for the fluid sample.
10. The apparatus of claim 1, further comprising wherein the tunable diode spectrometer perform measurements over the hydrocarbon band of frequencies, substantially from 1650-1850 nm.
11. A method for monitoring a parameter of interest for a down hole fluid sample comprising:  
containing a fluid sample in a chamber downhole; and  
  
spectrally analyzing the fluid sample with a tunable diode laser ultrahigh resolution spectrometer to determine a first parameter of interest for the fluid sample.
12. The method of claim 11, further comprising:  
separating vapor from liquid through a membrane for analysis of the vapor.
13. The method of claim 11, further comprising:  
analyzing a band of spectral frequencies of the fluid sample.
14. The method of claim 11, further comprising:  
shifting the wavelength of light from the TDL; and  
analyzing the Raman spectra of fluid sample using a single-wavelength detector.
15. The method of claim 11, further comprising:  
estimating a parameter of interest from the tunable diode laser spectrometer measurements using a soft modeling technique, such as a neural network, chemometric equation or least mean square fit.
16. The method of claim 13, wherein the wavelength of light entering into the sample is shifted and a single wavelength is detected.

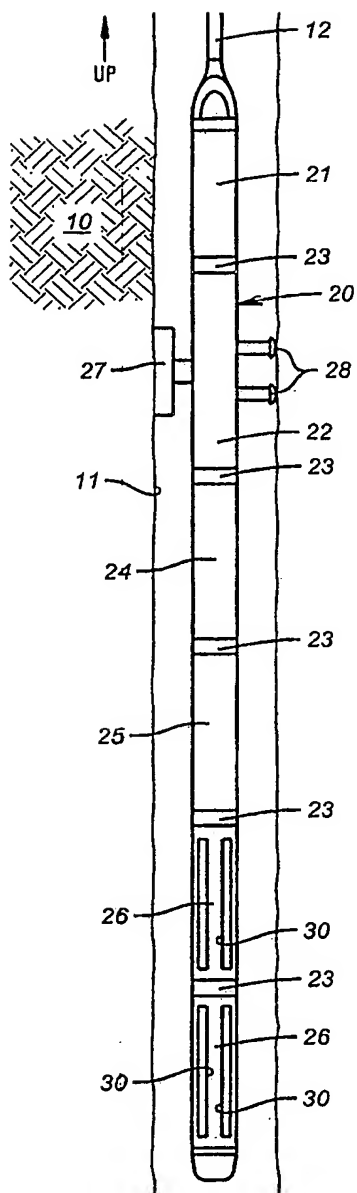
17. The method of claim 11, wherein the wavelength of the tunable diode laser is modulated for use as a derivative spectrometer.
18. The method of claim 11, further comprising:  
estimating a second parameter of interest for the fluid sample from a first parameter of interest of the fluid sample using a neural network.
19. The method of claim 11, further comprising:  
estimating a second parameter of interest for the fluid sample from the first parameter of interest for the fluid sample using a chemometric equation.
20. The method of claim 11, further comprising:  
spectrally analyzing the fluid sample by performing tunable diode spectral measurements over the hydrocarbon band of frequencies, substantially from 1650-1850 nm.
21. A computer readable medium containing computer instructions that when executed by a computer perform a method for monitoring a parameter of interest for a down hole fluid sample comprising:  
containing a fluid sample in a chamber downhole; and  
spectrally analyzing the fluid sample with a tunable diode laser ultrahigh resolution spectrometer to determine a first parameter of interest for the fluid sample.
22. The medium of claim 21, further comprising :  
separating vapor from liquid for analysis of the vapor.
23. The medium of claim 21, further comprising:  
analyzing the fluid sample over a band of spectral frequencies.
24. The medium of claim 21, further comprising:  
shifting the wavelength of light from a TDL; and



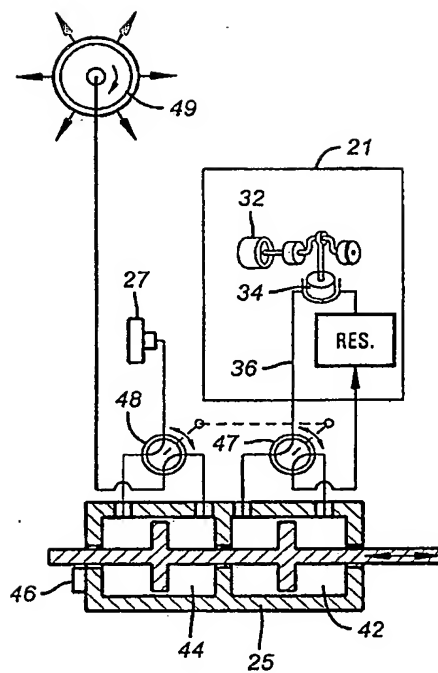
analyzing the Raman spectra of the fluid sample using a single-wavelength detector.

25. The medium of claim 21, further comprising:  
estimating a parameter of interest from the tunable diode laser spectrometer measurements using a soft modeling technique, such as a neural network, chemometric equation or least means square fit.
26. The medium of claim 23, wherein the wavelength of light entering the sample is swept while the Raman-shifted light at a single wavelength is detected.
27. The medium of claim 21, wherein the wavelength of the tunable diode laser is modulated for use as a derivative spectrometer.
28. The medium of claim 21, further comprising:  
estimating a second parameter of interest for the fluid sample from a first parameter of interest of the fluid sample using a neural network.
29. The medium of claim 21, further comprising:  
estimating a second parameter of interest for the fluid sample from the first parameter of interest for the fluid sample using a chemometric equation.
30. The medium of claim 21, further comprising:  
spectrally analyzing the fluid sample by performing tunable diode spectral measurements over the hydrocarbon band of frequencies, substantially from 1650-1850 nm.
31. An system for monitoring a parameter of interest for a down hole fluid sample comprising:  
a surface controller for deploying a downhole tool;  
a chamber in the downhole tool containing a fluid sample; and  
a tunable diode laser spectrometer for analyzing the fluid sample to determine a first parameter of interest for the fluid sample.

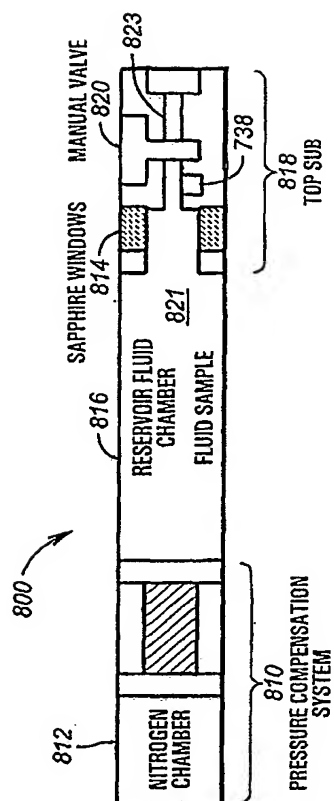
**FIG. 1**



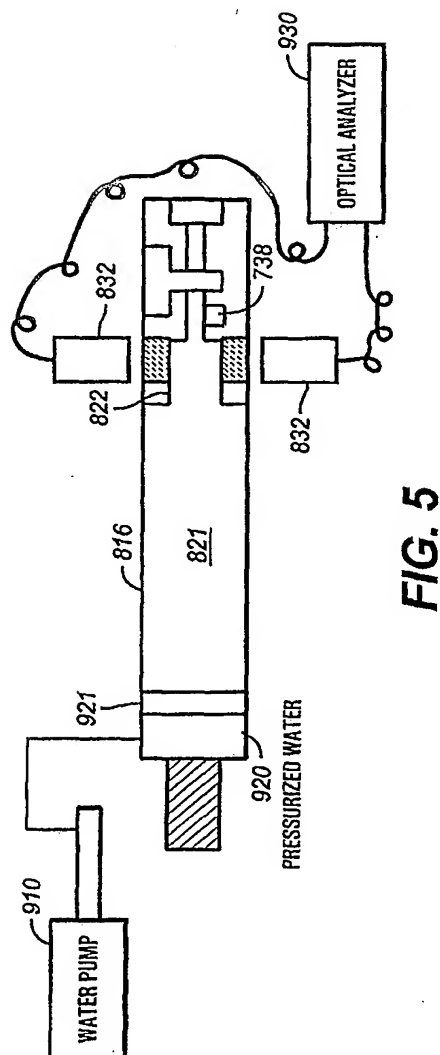
**FIG. 2**



**FIG. 3**



**FIG. 4**



**FIG. 5**

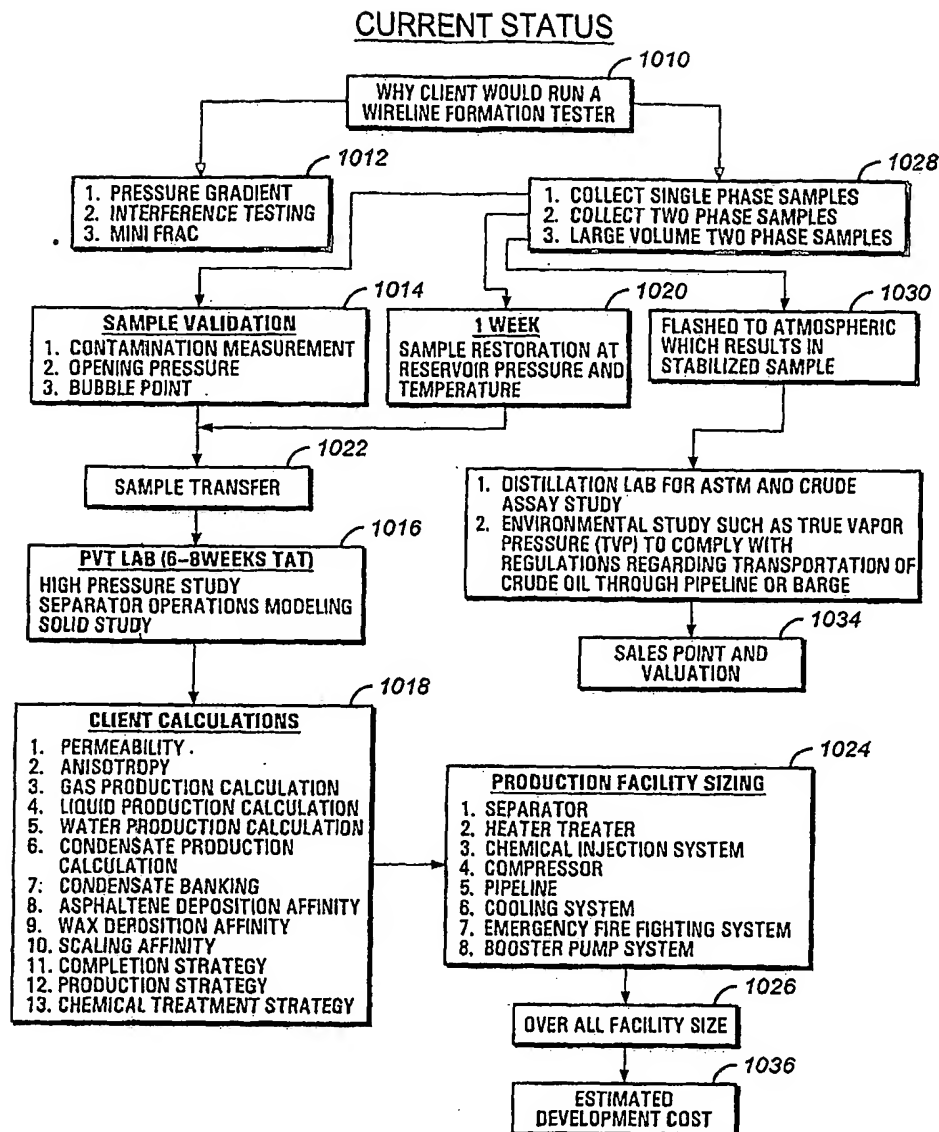


FIG. 6

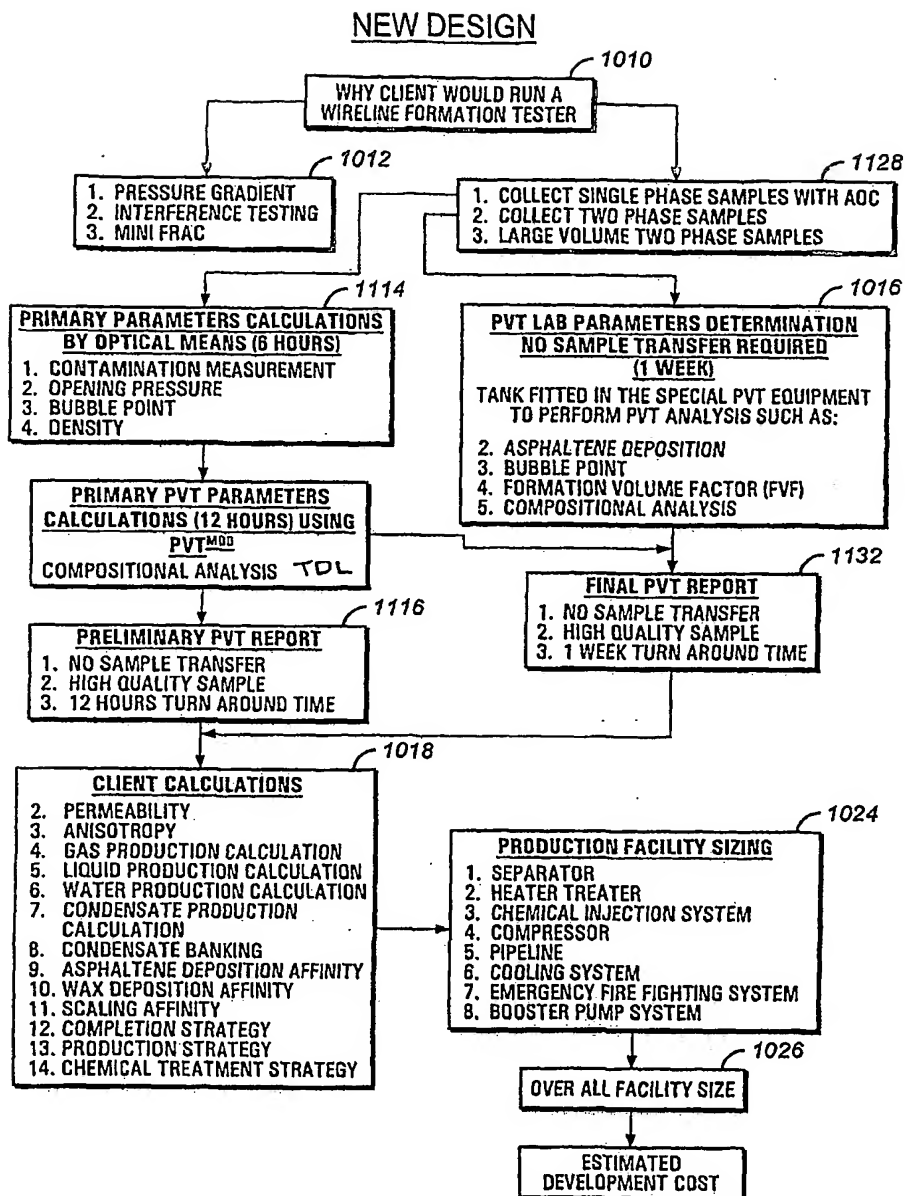
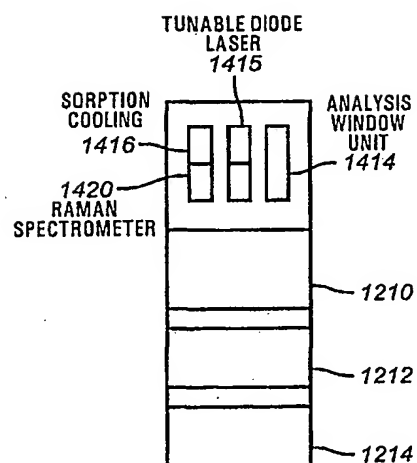
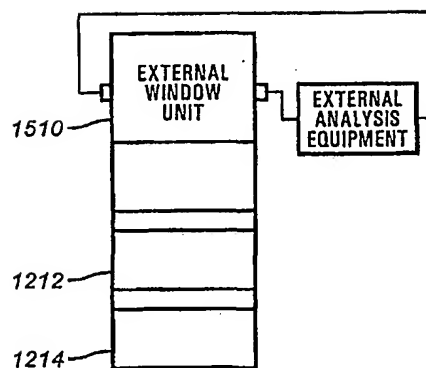


FIG. 7

**FIG. 8**



**FIG. 9**



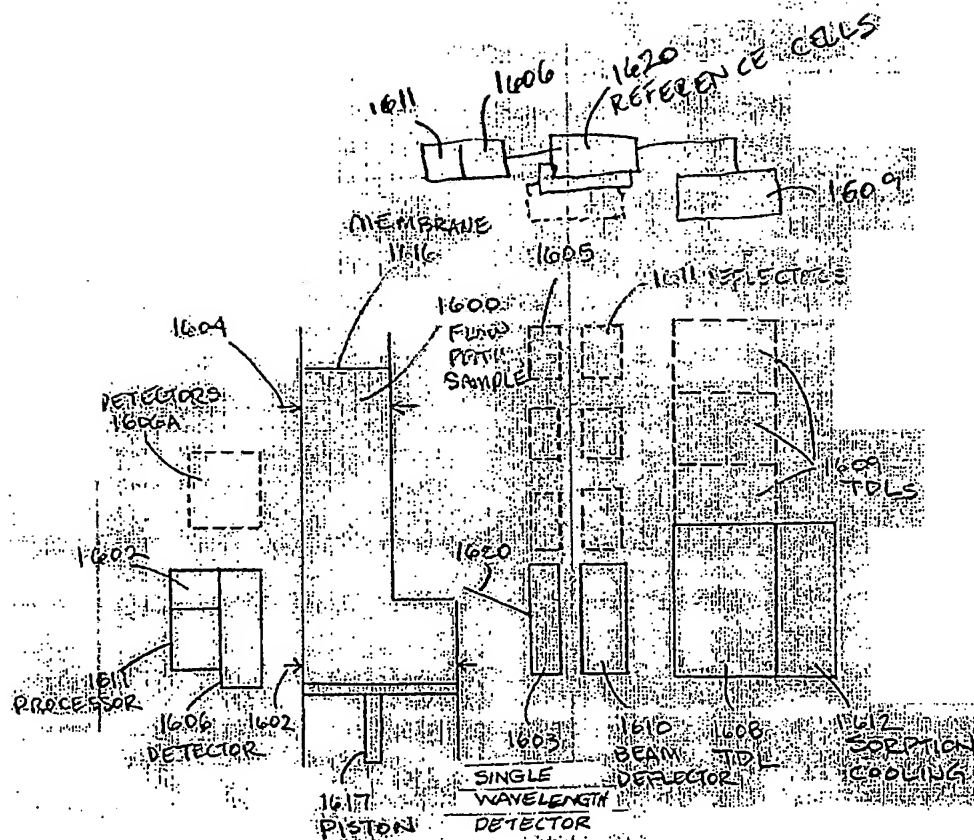


FIG. 10



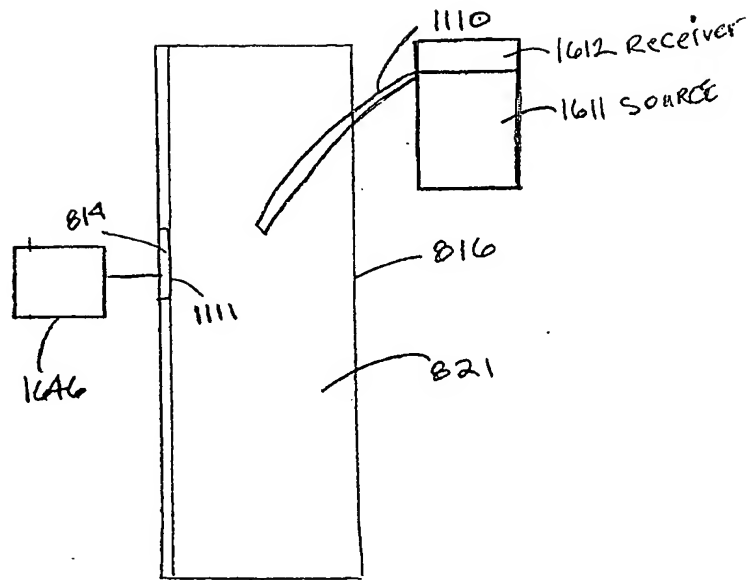


FIG 11

## PCT

REC'D 25 OCT 2004  
WIPO PC

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 584-34425-WO	<b>FOR FURTHER ACTION</b> see Form PCT/ISA/220 as well as, where applicable, Item 5 below.	
International application No. PCT/US2004/013887	International filing date (day/month/year) 05/05/2004	(Earliest) Priority Date (day/month/year) 06/05/2003
Applicant  BAKER HUGHES INCORPORATED		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ The international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the international application, see Box No. I.

2. ☐ Certain claims were found unsearchable (See Box II).

3. ☐ Unity of invention is lacking (see Box III).

4. With regard to the title,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

METHOD AND APPARATUS USING A TUNABLE DIODE LASER SPECTROMETER FOR ANALYSIS OF HYDROCARBON SAMPLES

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. With regards to the drawings,

- a. the figure of the drawings to be published with the abstract is Figure No. 1

☒ as suggested by the applicant.

☐ as selected by this Authority, because the applicant failed to suggest a figure.

☐ as selected by this Authority, because this figure better characterizes the invention.

- b. ☐ none of the figures is to be published with the abstract.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/013887

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 G01N21/39 G01V8/00 G02B26/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 937 448 A (MANTZ ARLAN W ET AL) 26 June 1990 (1990-06-26) column 4, line 10 - column 6, line 28 figure 2	1-31
A	US 6 064 488 A (BIEN FRITZ ET AL) 16 May 2000 (2000-05-16) column 2, line 40 - column 6, line 36 figures 1-3	1-31
A	US 5 317 156 A (RIRIS HARIS ET AL) 31 May 1994 (1994-05-31) column 2, line 55 - column 5, line 61 figures 1-4	1-31
	----- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents .

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

20 October 2004

Date of mailing of the international search report

26/10/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Modesto, C

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/013887

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 781 284 A (INFANTE DAVID A)  14 July 1998 (1998-07-14)  cited in the application  column 2, line 66 - column 10, line 36  figures 1-9</p> <p>-----</p>	1-31

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/013887

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4937448	A	26-06-1990	NONE
US 6064488	A	16-05-2000	NONE
US 5317156	A	31-05-1994	CA 2128607 A1 05-08-1993 DE 69320790 D1 08-10-1998 DE 69320790 T2 15-04-1999 EP 0624245 A1 17-11-1994 JP 7503319 T 06-04-1995 WO 9315391 A1 05-08-1993
US 5781284	A	14-07-1998	NONE

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**